On the Superlattice of Binary Alloys with a Large Unit Cell and of Many-Component Alloys. II : On the Superlattice of Many-Component Alloys

On the Superlattice of Binary Alloys with a Large Unit Cell and of Many-Component Alloys. II
On the Superlattice of Many-Component Alloys*

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Synopsis

Characteristic features of the superlattice formation in many-component alloys may be represented by those of ternary alloys in the usual formal theory. For this reason, general characteristics mainly about ternary alloys were argued here. The arguments were, in many points, similar to those of binary alloys with a large unit cell and the classification of superlattice was similarly made as before by introducing newly the definition of the distribution type of each sort of atoms. By extending the treatment of binary alloys to fit to ternary alloys, new feature appeared, which just corresponded to the appearance of the partial differentiation in the mathematical analysis because of many variables unlike the binary case in which only one variable was used. The conditions for the discrimination of the distribution of atoms were also generalized from this point of view and were found to be determined not only by the signs and the relative magnitudes of the interactions between every two constituents, but also by the number of equivalent sublattices and the concentrations of atoms. Stabilization of superlattice due to the splitting of Brillouin zones, which would be more important in many-component alloys than in binary case, was not referred to here.

I. Introduction

The superlattice in binary alloys has been studied comparatively well so far and its general characteristics seem to have become nearly clear. On the other hand, the superlattices of many-component alloys have scarecely been studied systematically because of many experimental difficulties. Furthermore, for a theoretical survey, the actual execution of numerical calculus is extremely tedious, because many variables are necessary. It is hoped, therefore, to have some guides for experimental studies to make clear the general characteristics of such problems without tedious calculations. For this purpose we shall examine some important points about the superlattice of many-component alloys according to the usual formal theory. To give a measure of the mode of atomic distribution in the superlattice of a many-component alloy, it is necessary to divide the crystal lattice into many sublattices and, therefore, such a superlattice will necessarily be classified as a superlattice with a large unit cell. For this reason the arguments are reduced to nearly the same as that of binary alloys given previously.(1)

* The 668th report of the Research Institute for Iron, Steel and Other Metals.

(1) H. Sato, Sci. Rep. RITU, **A 4** (1952), 1 (Hereafter we refer to this as I).

II. Problems concerning many-component alloys

To treat the problem of superlattice of many-component alloys, the unit cell must necessarily be enlarged, because we must arrange different atoms on different sublattices. Accordingly, we must apply to it the theory of the superlattice with a large unit cell given previously. Furthermore, some new factors arise from extending the treatment of the binary case to a many-component case.

As well known, the properties of a binary alloy is determined only by one parameter V which gives the relation of the interaction between constituent atomic pairs, where

$$V=\tfrac{1}{2}(V_{AA}+V_{BB})-V_{AB}. \tag{1}$$

In ternary alloys, on the other hand, we need three such parameters

$$\begin{aligned} V_1&=\tfrac{1}{2}(V_{AA}+V_{BB})-V_{AB},\\ V_2&=\tfrac{1}{2}(V_{BB}+V_{CC})-V_{BC},\\ V_3&=\tfrac{1}{2}(V_{CC}+V_{AA})-V_{CA}. \end{aligned} \tag{2}$$

(Even in ternary alloys, in the case of the addition of the third element to the binary alloys, for an example, only the ratios of every two of these are necessary and, consequently, the properties of alloys are determined by two variables.[2]) New facts thus appear just correspondingly to the appearance of the partial differentiation in the mathematical analysis in the case of many variables when we extend the arguments from a binary case to a ternary case. As no new characteristic appears by extending the treatment from two variables to many variables in methematical analysis, new special circumstances will not appear also in many-component system. In this sense, a ternary alloy may be a miniature of a many-component alloy and we may infer the characteristics of the latter by studying the ternary alloys. The importance of a ternary alloy for general studies of superlattice lies in this point.

Apart from a mathematical expression, some main features corresponding to the above new facts will qualitatively be given below.

1. When the third element C is added to the alloy AB by replacing the atoms B, two cases will be possible: either C enters into the site B and does not derange the relation of sublattices concerning A and B, or C enters into the site A by replacing the atom A and derange the relation between A and B. The grounds for these two cases depend not only on the sign of each parameter but also on the relative magnitudes among them, and cannot be concluded so simply as in the binary case. (cf. the later chapter) Here we may say that in the former case C enters into AB *constructively* and in the latter case C enters *destructively*. As an example of the constructive case we may point out $Fe_3(Al_{1-x}\ Si_x)$, in which atoms Si replace atoms Al at random along the composition line from Fe_3Al to Fe_3Si.[3]

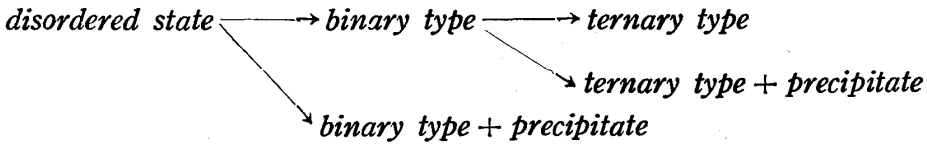
2. A case of simultaneous occurrence both of ordering and segregation may be

(2) T. Hirone, T. Katayama, Bulletin of the Inst. Phys. Chem. Research 21 (1942), 992.
(3) H. Sato and H. Yamamoto, J. Phys. Soc. Japan 6 (1951), 65.

considered. For example, three components, which are mutnally soluble in a disordered state, show either a regular arrangement with the composition near the certain binary superlattice or a ternary superlattice of specific composition, and separate the remaining elements at lower temperatures. This case may be termed the *separative type.*

3. *A*, *B* and *C* are arranged on their own sublattices, respectively. Such as Heusler alloy, Cu_2MnAl,[4] belongs to this case. This third case is the typical ternary superlattice and may be termed the *ternary type superlattice.* On the other hand, the superlattice which retains the symmetry of binary superlattice may be termed the *binary type superlattice.* Such nomenclatures may similarly be extended to many-component case. A ternary type superlattice, furthermore, needs more sublattices for its description than a binary type and corresponds to the higher order superlattice defined previously.[1] If the other conditions are fixed, therefore, it will have to appear at lower temperatures.

From such a point of view, in ternary alloys, it will be anticipated that there will be not only the disordered state and the ordered state but also many types of states which will appear at different temperature ranges as mentioned above. For example, the state changes as in the following schema.



Naturally, not in all cases, each stage must stepwise be passed through as shown before[1] and there may also be cases where atoms arrange orderly in the precipitate. All such behaviours depend on the respective signs and the relative magnitudes of the parameters, the type of crystal lattice and the concentration of each kind of atom.

In ternary alloys, we can thus classify the superlattice by introducing the definition of distribution type of each sort of atom along with the order of superlattice. Heusler alloy may be termed, for example, the ternary, ternary type, second order superlattice Cu_2MnAl, in the b. c. c. lattice and $Fe(Al_{1-x}Si_x)$ is termed the ternary, binary type, second order superlattice, in the b. c. c. lattice. Although we proceed to many-component alloys, the relation will be expressed similarly if we extend such type of classification correspondingly.

III. Statistical mechanical treatment of many-component alloys

As the treatment of many-component alloys may be represented by that of ternary alloys, here we will restrict ourselves to the ternary case. It will easily be understood that the argument proceeds in quite parallel as in the case of the binary alloy with a large unit cell. The representation may thus be abbreviated by referring to the arguments in I.

(4) A. J. Bradley and J. W. Rodgers, Proc. Roy. Soc. **144A** (1934) 340.

Denote three elements by A, B and C and define several quantities by the same symbols as in I-V, then the number of each atom on each sublattice may be specified as follows:

$$\begin{aligned}
[A/pm+q] &= \frac{N}{n}\,\frac{1+\alpha_{pm+q}}{2}, \\
[B/pm+q] &= \frac{N}{n}\,\frac{1+\beta_{pm+q}}{2}, \\
[C/pm+q] &= \frac{N}{n}\,\frac{1+\gamma_{pm+q}}{2}.
\end{aligned} \tag{3}$$

The energy of the system is, if we restrict the interaction energy only to the nearest neighbouring pairs, given by B. W. approximation, or

$$\begin{aligned}
E = {} & \frac{N}{n} z_1 \frac{1}{2} \sum_p \left[\sum_q \frac{1+\alpha_{pm+q}}{2} \right] \left[\sum_{p' \neq p} \sum_{q'} \frac{1+\alpha_{p'm+q'}}{2} \right] V_{AA} \\
& + \frac{N}{n} z_1 \frac{1}{2} \sum_p \left[\sum_q \frac{1+\alpha_{pm+q}}{2} \right] \left[\sum_{p' \neq p} \sum_{q'} \frac{1+\beta_{p'm+q'}}{2} \right] V_{AB} \\
& + \frac{N}{n} z_1 \frac{1}{2} \sum_p \left[\sum_q \frac{1+\alpha_{pm+q}}{2} \right] \left[\sum_{p' \neq p} \sum_{q'} \frac{1+\gamma_{p'm+q'}}{2} \right] V_{AC} \\
& + \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots \quad \cdots .
\end{aligned} \tag{4}$$

Entropy Φ is given by $\Phi = k \ln W$ and

$$W = \prod_p \prod_q \frac{\left[\frac{N}{n}\right]!}{\left(\frac{N}{n}\,\frac{1+\alpha_{pm+q}}{2}\right)! \left(\frac{N}{n}\,\frac{1+\beta_{pm+q}}{2}\right)! \left(\frac{N}{n}\,\frac{1+\gamma_{pm+q}}{2}\right)!} . \tag{5}$$

The free energy, then, becomes additive of that of each nearest neighbouring sublattice group quite similarly as in the binary case and

$$F = \sum_p F_p \tag{6}$$

may be obtained. Here

$$F_p = E_p - kT \ln \prod_q \frac{\left(\frac{N}{n}\right)!}{(\alpha)!\,(\beta)!\,(\gamma)!} . \tag{7}$$

$(\alpha)!$, etc. are the abbreviations of $\left(\frac{N}{n}\,\frac{1+\alpha_{pm+q}}{2}\right)!$, etc.

On the other hand, as there are restrictions

$$\begin{aligned}
\frac{N}{n} \sum_p \sum_q \frac{1+\alpha_{pm+q}}{2} &= NC_A \\
\frac{N}{n} \sum_p \sum_q \frac{1+\beta_{pm+q}}{2} &= NC_B \\
\frac{N}{n} \sum_p \sum_q \frac{1+\gamma_{pm+q}}{2} &= NC_C,
\end{aligned} \tag{8}$$

(C_A, C_B, etc. are the concentrations of A atoms, B atoms, etc.), and it follows

$$\sum_{p' \neq p} \sum_{q'} \frac{1+\alpha_{p'm+q'}}{2} = NC_A - \sum_q \frac{1+\alpha_{pm+q}}{2} , \text{ etc.} . \tag{9}$$

Furthermore as

$$\frac{1+\gamma_{pm+q}}{2}=1-\left(\frac{1+\alpha_{pm+q}}{2}+\frac{1+\beta_{pm+q}}{2}\right)$$
$$=-\left(\frac{\alpha_{pm+q}+\beta_{pm+q}}{2}\right), \tag{10}$$

the independent different parameters giving the distribution of atoms are only $\sum_q \alpha_{pm+q}$ and $\sum_q \beta_{pm+q}$. The problem of finding the minimum of F is thus reduced to that of finding the minimum of F_p as in the binary case.

Further, as

$$\frac{\partial E}{\partial \alpha_{pm+q}}=\frac{\partial E}{\partial \alpha_{pm+q'}}, \qquad \frac{\partial E}{\partial \beta_{pm+q}}=\frac{\partial E}{\partial \beta_{pm+q'}} \tag{11}$$

are obtained, we can obtain

$$\frac{\partial \Phi_p}{\partial \alpha_{pm+q}}=\frac{\partial \Phi_p}{\partial \alpha_{pm+q'}}, \quad \text{etc.}, \tag{12}$$

as the equilibrium condition. Finally, we can obtain

$$\alpha_{pm+q}=\alpha_{pm+q'}, \quad \beta_{pm+q}=\beta_{pm+q'} \tag{13}$$

quite similarly as before. In the ternary alloys, therefore, we can also discuss the equilibrium state by calculating only one combination of parameters $(\alpha_{pm+q}, \beta_{pm+q})$ as far as we take only the nearest neighbour interaction. More generally, in many-component alloys, it will be deduced that for one parameter in binary case one combination of parameters, the number of which is less than the number of components by one, corresponds. The correspondence is quite similar also when we take into consideration the interaction of the second order, third order, etc.. According to the different values which this combination may have, the type of superlattice realized is determined. Thus the argument is advanced forward quite in parallel as in the binary alloys and it becomes clear that the classification of many-component superlattice becomes possible by supplementing newly the arrangement type of each component as compared to the binary case.

IV. Relations between interaction parameters and type of superlattice

In binary alloys, the criterion whether the alloy forms superlattice or separates depends solely on the sign of V. In many-component alloys, however, many types appear mixed together and there is no such simple criterion as in binary alloys. The behaviours of the alloy cannot be determined only by the signs of $V_1, V_2, \cdots$. It is necessary, therefore, to examine the systematic measure for the type appearing in many-component alloys, in order to make clear the origin of the appearance of the different types aforementioned or of their mixing. We will try to attain this object by comparing the many-component case with the binary case and then by extending the criterion in binary alloys to fit to the former case.

Let the parameters representing the interaction between atoms be $V_1, V_2, \cdots\cdots$, and the numbers of pairs of corresponding sorts of different atoms be $Q_1, Q_2, \cdots\cdots$.

In the binary case, V_i is only one and is equal to V, and the corresponding Q_i is Q_{AB}. The configurational energy of the alloy is the total sum of the pairs of atoms and this may be rearranged and rewritten in order to fit to the object as follows:

$$E=-\sum_i V_iQ_i+N\sum_i V^iC_i\ ,\quad \sum_i C_i=1\ . \tag{14}$$

V^i represents the interaction energy of the pair of similar atoms of i sort and C_i denotes the concentration of the corresponding atoms. It may be clear that this equation holds good also for the case in which the alloy separates. In the binary case, for example, V^i's represent V_{AA} and V_{BB}, respectively, and C_i's the concentrations of atoms A and B, namely C_A and C_B. As the second term of (14) is an additive constant which is determined by the concentration of atoms, the configurational energy is a linear function of V_i, the coefficient of which is the number of corresponding pairs of atoms Q_i, when the concentration of atoms is fixed. We have adopted V_i's as variables so far, but it is more convenient to take Q_i's as variables, which are equivalent to V_i's in the meaning of (14), when we treat the energy change due to the change of the atomic arrangement or of the concentration of atoms, the sort of elements of the alloy being fixed. Thus in the former case we may write

$$dE=\sum_i \frac{\partial E}{\partial Q_i}dQ_i\ . \tag{15}$$

On the other hand, as we have from (14)

$$\frac{\partial E}{\partial Q_i}=-V_i\ ,$$

we can obtain

$$dE=\sum_i -V_idQ_i\ . \tag{16}$$

As V_i's are fixed by the assumption, the energy surface of the alloy is a hyperplane in the Q_i-E space. As the possible existence range of Q_i is determined in this plane, including the case of precipitation, according to the type of crystal lattice and the composition of atoms, the lowest point in this region thus corresponds to the arrangement of atoms at the absolute zero of temperature. What is composed together with the entropy surface will specify the state at each temperature.

Let us first consider the binary case. In this case (16) becomes

$$dE=\frac{dE}{dQ_{AB}}dQ_{AB}=-V\cdot dQ_{AB}\ . \tag{17}$$

In order to get to a more stable state, $dE<0$ must hold and the sign of dQ_{AB} is determined according to the sign of V. In other words, the signs of V and dQ_{AB} corresponds to each other, and in the case where V is positive it is more stable when Q_{AB} increases. In the case of a first order superlattice, the relation between E and Q_{AB} is a straight line and $Q_{AB}=0$ corresponds to the complete separation and $(Q_{AB})_{\max.}$ corresponds to the completely ordered state. Therefore, if $dQ_{AB}>0$, the state of $(Q_{AB})_{\max.}$ is the energetically lowest state and the alloy forms superlattice and, if $dQ_{AB}<0$, the $Q_{AB}=0$ is the lowest and the alloy separates.

The fact that Q_{AB} cannot be decreased below the value of the completely disordered state without separation, admitting the decrease in Q_{AB} due to the formation of short range group formation, along with the fact that in this case the variable is only one, becomes the ground for the fact that the sign of V separates the phenomena sharply into two in this case. This will be referred to afterwards from a general point of view.

In the case of a ternary alloy, we have

$$dE=\frac{\partial E}{\partial Q_{AB}}dQ_{AB}+\frac{\partial E}{\partial Q_{BC}}dQ_{BC}+\frac{\partial E}{\partial Q_{CA}}dQ_{CA}$$
$$=-(V_1dQ_{AB}+V_2dQ_{BC}+V_3dQ_{CA})\ . \qquad (18)$$

It is through this form that the many-component alloy manifests new features corresponding to the partial differentials mentioned above. It is to be noted that V_1, V_2 and V_3 need not be all positive in order that $dE<0$, and it will be clear that the lowest value of (18) is determined by both the signs and relative magnitudes of V_i's and dQ_i's. Also we can decrease one of Q_i's below the value of random distribution without separation, according to the type of crystal lattice and to the concentration of atoms. In the superlattice with the stoichiometric composition AB with two equivalent sublattices, in such as b. c. c. lattice or s. c. lattice, for example, we can make $Q_{BC}=0$ in the case in which we replace atoms B with atoms C and if all atoms C enter into the sites B. From this fact, we can understand that both the signs of V_i's and the numbers of Q_i's are necessary for the criterion. We divide the conditions, therefore, into two as follows:

i) A limit is imposed on the number of Q_i's in order that $dE\leqq 0$, according to the signs and the magnitudes of V_i's. We may call this the *limitation of V*. In the binary case, that $dQ_{AB}>0$ is the condition for $dE<0$ when $V>0$, means the limitation of V imposed on Q_{AB}.

ii) Though the signs of dQ_i's are determined, because of the limitation of V, there is a limiting range in the attainable values of Q_i's. In the binary case, for example, we cannot make the value of Q_{AB} less than the value of a completely disordered state without separation, if we neglect the decrease due to the short range group formation. In a ternary case, or further in a many-component case, we not only can decrease the value of one of Q_i's, but even make it zero as in the above example. We now consider a first order superlattice. If the number of the sorts of elements ν is greater than the number of equivalent sublattices of first order, P_1, i. e.

$$P_1<\nu \qquad (19)$$

there is a possibility for Q_i to decrease below the value of the disordered state, and if the number of two elements concerned, $N(C_i+C_k)$, is smaller than the number of lattice points in one of the sublattice, N/P_1, i. e.

$$N/P_1>N(C_i+C_k) \quad \text{or} \quad 1/P_1>C_i+C_k\ , \qquad (20)$$

we can make Q_i zero. As easily understood from (18) and (19), there is a limit in the attainable values of Q_i's and we call this the *limitation of Q*. In the binary case, the limitation of Q, (19), does not hold, because in this case $\nu=2$ and $P_1\geqq 2$.

In the binary case, therefore, the limitation of V and the limitation of Q are not independent of each other and the state is determined only from the limitation of V. Along with the fact that the variable is only one, the state is decidedly specified only by V in the binary case. That the limitation of V and that of Q may be mutually independent is one of the characteristics of many-component alloys.

The measure of the distribution of atoms in many-component alloys is understood to be given by the limitation of V and that of Q (15), (19) and (20), and a definite measure does not exist as in a binary case. The distribution of atoms must be, therefore, determined according to the type of crystal lattice and the concentration of atoms. We will take a qualitative example in the ternary case to show how these conditions may appear as in the several types mentioned above.

1) The case in which the concentrations of atoms are constant

The precipitation and the superlattice formation cannot easily be separated, and which of these cases is to appear is determined only by a scarce difference in the limitation of V and the limitation of Q. To this case the following two cases belong:

i) homogeneous case; *binary type, ternary type (many-component type)*

ii) inhomogeneous case; *separative type.*

Binary type and *separative type* are rather similar in meaning. Even if the limitation of V is the same, it separates into either inhomogeneous or homogeneous case depending upon whether or not the limitation of Q, (19) and (20), are fulfilled. If we take into account the entropy relation which mitigates the limitation of Q, therefore, these two different types, which are not compatible in the binary case, may exist in the alloy with the determined concentration in the different range of temperature. In order to compose the *ternary type*, the decrease in the energy is necessary due to the increase in Q_{AB}, Q_{BC} and Q_{CA} at the given concentration. The necessary conditions are, therefore,

i) necessary numbers of sublattices for the distribution of each element exist, i. e.

$$P_1 \geqq \nu$$

holds, (limitation of Q) and

ii) V_1, V_2 and V_3 are all positive. (*limitation of V*)

These are, however, not sufficient conditions. The criterion whether the alloy retains in binary stage or it further composes *many-component type* (*ternary type*) is easily given in the case where the alloy does not separate.

2) The case in which the concentrations of atoms change

We take the case in which the third element is added to the binary alloy. In this case we have, as indicated before, two different types,

i) constructive type

and

ii) destructive type.

In order to determine which type will appear only from the relation of V's, the

limitation of Q must be fixed. As one of the simplest cases, we shall take a binary superlattice of first order with stoichiometric composition AB. Then we replace atoms B with atoms C. From the definition of constructive type, we can take

$$[dQ_{AB}]^1=[dQ_{CA}]^1 \tag{25}$$

and

$$dQ_{BC}=0\,.$$

The energy change is thus

$$dE=-\{(V_3-V_1)[dQ_{AB}]^1\}-N(V_{BB}-V_{CC})dC_C. \tag{26}$$

In the case of destructive type, on the other hand, atoms C enter in A sites and

$$-[dQ_{AB}]^2=[dQ_{CA}]^2+[dQ_{BC}]^2. \tag{27}$$

We obtain thus

$$dE=-\{-V_1[dQ_{AB}]^2+V_2[dQ_{BC}]^2+V_3[dQ_{CA}]^2\}-N(V_{BB}-V_{CC})dC_C. \tag{28}$$

The reason why we attach the superscript 1 or 2 to the dQ_{AB}, etc. is to distinguish the change in the number of pairs in these two cases. In the above case, however, we may put, in the degree of approximation of B. W.,

$$[dQ_{AB}]^1=[dQ_{AB}]^2=dQ_{AB}\,, \tag{29}$$

and the energy difference between these two cases is

$$-\{V_3dQ_{AB}-V_2[dQ_{BC}]^2-V_3[dQ_{CA}]^2\}\,. \tag{30}$$

On the other hand,

$$\begin{aligned} &dQ_{AB}=NzdC_C\,,\\ &[dQ_{BC}]^2=NzdC_C-2Nz(dC_C)^2, \end{aligned} \tag{31}$$

and

$$[dQ_{CA}]^2=2Nz(dC_C)^2$$

hold and (30) becomes

$$-NzdC_C\{V_3V_2(1-2dC_C)-2V_3dC_C\}=-NzdC_C(V_3-V_2)(1-2dC_C).$$

As it is assumed that $2dC_C\leqq 1$ holds, the type to appear is determined according to the sign of V_3-V_2. The criterion will thus easily be given in any case concerned according to the type of crystal lattice and the concentration of atoms.

Such discussions are also applicable to the case in which we take into account the interaction between second nearest neighbours or further.

As the unit cell is necessarily enlarged in the superlattice of many-component alloys, the rôle played by the stabilization of superlattice due to the splitting of Brillouin zones will be more important than in binary case and will have many applications. In such a case, the number of electrons per atom and the symmetry of crystal lattice are to considered for the problem. As for particular problems, let us defer them until the time when it is necessary.

Summary

General characteristics of superlattice in many-component alloys were discussed from the standpoint of a formal theory. Main conclusions were as follows:

i) Mainly the properties of ternary alloys were discussed because the general properties of many-camponent alloys were represented by those of ternary alloys.

ii) As the unit cell was enlarged in a many-component case, the conclusions were nearly the same as those of binary alloys with a large unit cell. The classifications and the nomenclature of superlattice type of many-component alloys could thus be done similarly only with a somewhat more complexity compared with those of binary alloys.

iii) New features corresponding to the partial differentiation appeared because of the increase in variables.

iv) By extending the treatment of binary case, criterions on the type to appear in the ternary case were given. In many-component alloys, the limitation of V and that of Q were mutually independent.

v) Above conclusions did not hold if the assumption made about the ordering energy were not fulfiled. The difference between the above conclusions and the properties of actual alloys thus gave some clue to the study of the mechanism of cohesion of alloys concerned.

As for the stabilization due to the splitting of Brillouin zones which are considered to be more important in many-component case than in binary case, we shall defer its explanation and application until the time when it is necessary.